NICKELOCENE-LITHIUM ALUMINUM HYDRIDE-A NEW EFFECTIVE DESULFURIZATION REAGENT

CHENG KWOK-MAN

(鄭國文)

A thesis submitted in partial fulfilment of the requirements for the degree of Master of Philosophy in The Chinese University of Hong Kong

1986

Thesis Committee:

Dr. Tien-Yau Luh, Chairman

Dr. Choi Nang Lam

Dr. Henry N. C. Wong

Prof. Xiyan Lu, External Examiner

ACKNOWLEDGMENTS

I am indebted to Dr. T.-Y. Luh for his guidance, discussions and opinion in the research work and the preparation of this thesis.

I am grateful to Messrs. M. C. Chan and N. F. Ho for assistance and to Messrs. Y. H. Law, C. W. Fung and K. W. Kwong for carrying out nmr and mass spectral measurements. Thanks are also due to Mr. A. Birch and Ms. Y. O. Lam of Dow Chemical (HK) Ltd. for the arrangement and measurement of FT-IR data and to Dr. F. T. Chau of Hong Kong Polytechnic for X-ray fluorescence measurements.

This work was partially supported by the Croucher Foundation.

CHENG KWOK-MAN
Department of Chemistry
C.U.H.K.
July 4, 1986.

CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

ABSTRACT

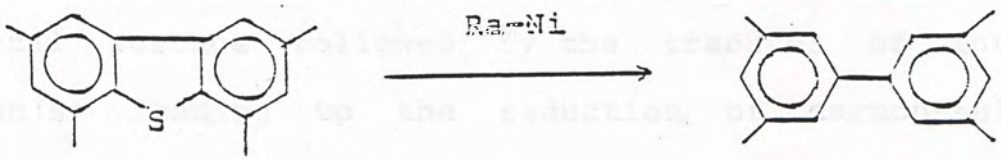
A new homogeneous organonickel reagent prepared from nickelocene and lithium aluminum hydride has been shown to be effective for the reduction of carbon-sulfur bonds to the corresponding carbon-hydrogen bonds. Alkyl, aryl or benzylic mercaptans or sulfides are readily reduced in moderate to good yields. Functional groups such as olefinic double bonds, esters, carbonyls, halides remain intact under the reaction conditions. Preliminary studies on the nature of the reagent and the mechanisms for these reactions have been carried out by employing deuterium labeling experiments and nmr as well as ir techniques. It is believed that metal hydridic species may play an important role for the reduction of carbon-sulfur bond. The reaction behavior of this newly developed nickel reagent parallels to that of Raney nickel. Hence, the reagent may serve as a homogeneous model for understanding various reactions promoted by the latter heterogeneous reagent.

INTRODUCTION

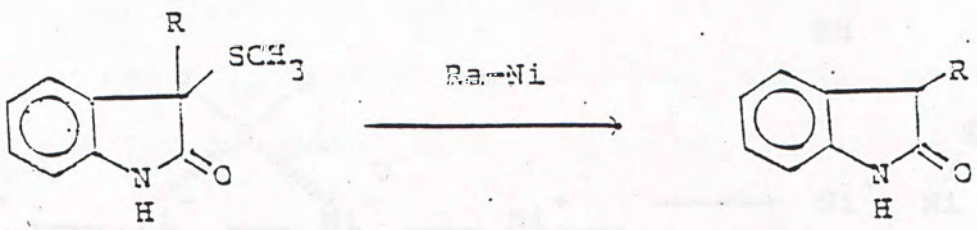
The use of organosulfur compounds in organic synthesis is well-documented.[1-3] The general practice in this area of chemistry often involves the reduction of the carbon-sulfur bond to the corresponding carbon-hydrogen bond.[1-3] Examples are shown in eqs. 1-4.

$$Ph_2CH(OH)CH_2SH \xrightarrow{Ra\text{-}Ni} Ph_2CH(OH)CH_3 \qquad (1)^{4}$$

(2)[5]



(3)[6]



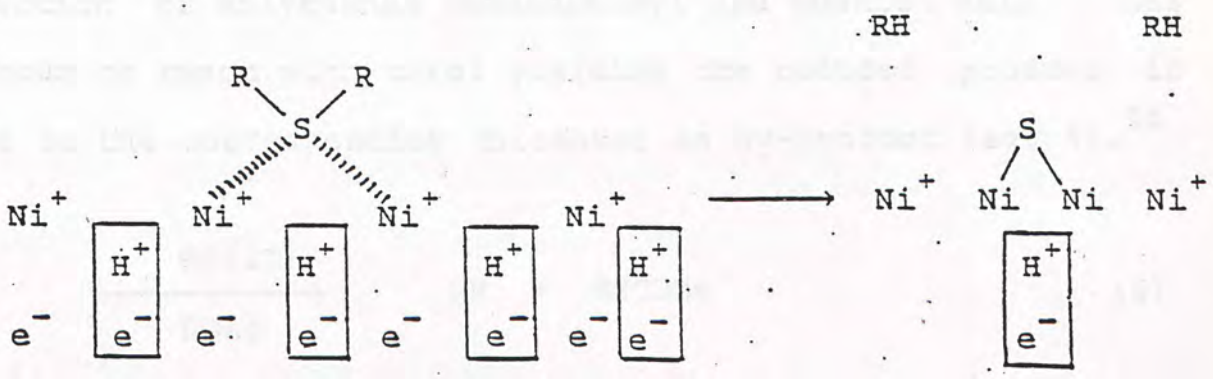
(4)[7]

In these reactions, Raney nickel,[8] a widely used desulfurization agent, has been employed for the reductive cleavage of carbon-sulfur bond. The mechanism for this important reaction, however, is not well-understood. A free radical mechanism has been proposed (Scheme 1).[9] It is noted that the

$$R\text{-}S\text{-}R + Ni\cdot \longrightarrow R\cdot + Ni\text{-}S\text{-}R$$
$$R\cdot + H(\text{adsorbed}) \longrightarrow RH$$
$$2R\cdot \longrightarrow R\text{-}R$$

Scheme 1

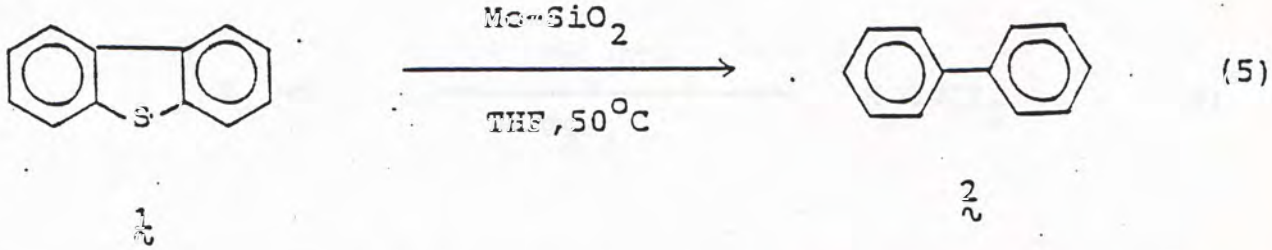
hydrogen source for this mechanism may arise from some kind of adsorbed hydrogen on metallic surface.[9] However, no direct evidence to support this suggestion has been reported. More recently, Horner and Doms proposed an alternative mechanism for the Raney nickel promoted desulfurization reaction.[10] They suggested that organosulfur compounds may first be adsorbed on the metal surface followed by the transfer of interstitial hydrogen(s) leading to the reduction of carbon-sulfur bond (Scheme 2). However, the actual mode of the carbon-sulfur cleavage process is still not clear.



Scheme 2

Hydrodesulfurization, a process involving the removal of sulfur contents from crude oil or coal, is one of the most active research areas in chemical industry.[11] The commonly used catalyst for this reforming process consists of molybdenum sulfide supported on aluminum oxide with cobalt or nickel compounds as promoter. Extensive studies on this system have been carried out.[11] Like Raney nickel promoted reactions, the mechanism for this heterogeneous reaction remains unclear.

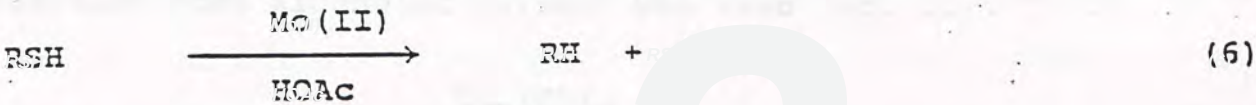
One approach to tackle this type of problem is to develop a homogeneous organometallic system to simulate the heterogeneous reaction.[12] There are a few organometallic reagents which can reportedly reduce the carbon-sulfur bond. To illustrate, activated molybdenum on silica gel was found to be active for the conversion of dibenzothiophene (1) to biphenyl (2) as shown in eq. 5.[13]



(5)

1 2

Alternatively, molybdenum(II) complex generated in situ from the reaction of molybdenum hexacarbonyl and acetic acid[14] has been shown to react with thiol yielding the reduced product in addition to the corresponding thioester as by-product (eq. 6).[15]

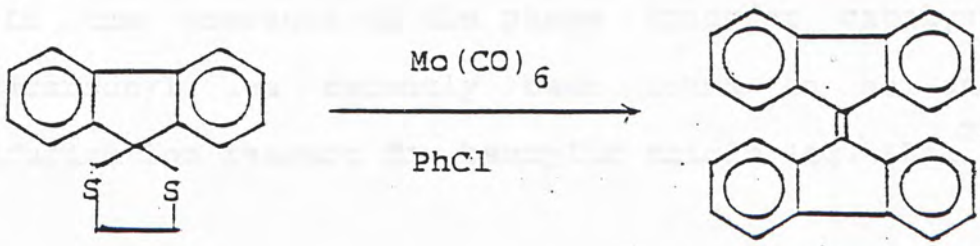


(6)

Recently, Luh and Wong reported that molybdenum hexacarbonyl itself in refluxing THF is a selective reducing agent for the reductive cleavage of the carbon-sulfur bond (eq. 7).[16] When chlorobenzene was employed as solvent, the thioketal 3 was transformed into bifluorenylidene (4) in moderate yield as outlined in eq. 8.[17]

$$R\text{-}S\text{-}R' \xrightarrow[THF]{Mo(CO)_6} RH + R'H \qquad (7)$$

R,R' ≠ Alkyl



(8)

3 4

A homogeneous desulfurization reaction using dicobalt octacarbonyl was reported by Alper and his coworkers (eqs. 9 and 10).[18,19]

$$R_2C{=}S \xrightarrow[C_6H_6]{Co_2(CO)_8} R_2C{=}CR_2 \qquad (9)$$

$$RSH + CO \xrightarrow[H_2O,C_6H_6]{Co_2(CO)_8} RH + COS \qquad (10)$$

On the other hand, esters were obtained from the latter reaction when alcoholic solvent was used (eq. 11).[20]

$$RSH \xrightarrow[H_2O/C_2H_5OH]{Co_2(CO)_8} RCOOC_2H_5 \qquad (11)$$

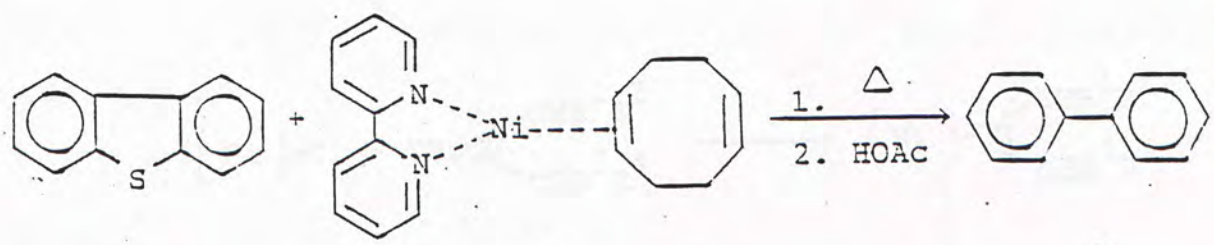
In contrast to cobalt-promoted reactions, treatment of thioketones with iron pentacarbonyl afforded the corresponding reduced products (eq. 12).[18,21] The active species would presumably be hydridotetracarbonylferrate anion.[21]

$$R_2C{=}S \xrightarrow[KOH]{Fe(CO)_5} R_2CH_2 \qquad (12)$$

In the presence of the phase transfer catalyst, triiron dodecacarbonyl has recently been found to be an efficient desulfurization reagent for benzylic thiols (eq. 13).[22]

$$R_1R_2R_3CSH \xrightarrow[(C_4H_9)_4NHSO_4,\ OH^-,C_6H_6]{Fe_3(CO)_{12}} R_1R_2R_3CH \qquad (13)$$

Eisch and his coworkers have studied the desulfurization of 1 with the nickel(0) complex 5 as indicated in eq. 14.[23] Biphenyl 2 was obtained in moderate yield from this reaction; but the



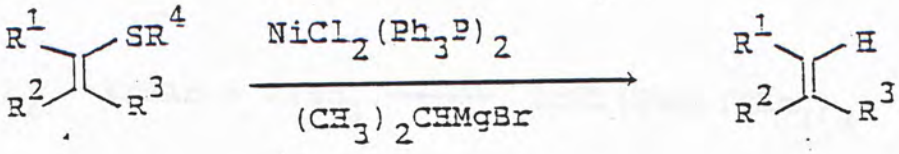
(14)

1 5 2

yield was significantly improved when lithium aluminum hydride was introduced to this reaction. A nickel hydride intermediate was suspected.[23]

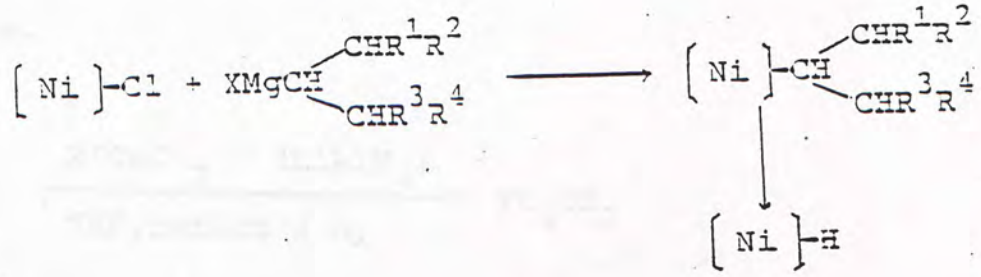
A facile substitution of alkylthio groups on olefins and arenes by alkyl or aryl functions in reactions with primary or aryl Grignard reagents, under catalysis of low valent nickel species has been reported (eq. 15).[24] On the other hand, reduction of the carbon-sulfur bond has been claimed when secondary Grignard reagents were employed (eq. 16).[25]

$$CH_3(CH_2)_5CH{=}CHSCH_3 \xrightarrow[CH_3MgBr]{NiCl_2(Ph_3P)_2} CH_3(CH_2)_5CH{=}CHCH_3 \qquad (15)$$



(16)

The mechanism for the latter reaction has not been fully explored. It is likely that Grignard reagent may first displace the chloride to form the corresponding metal-alkyl which may undergo ß-elimination yielding nickel hydride (Scheme 3).[26] Such retrograde insertion reaction would particularly be facile for the sterically crowded metal-alkyls.[26]



Scheme 3

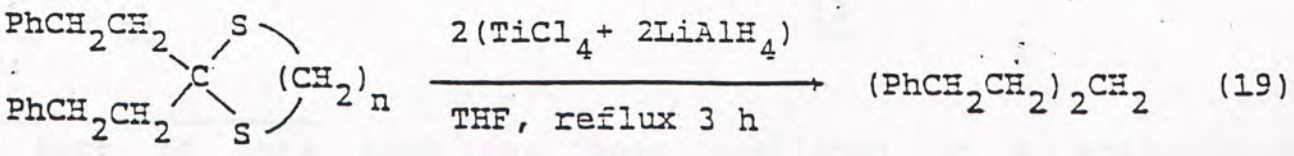
Recently, the carbon-sulfur bond in diaryl sulfide has been shown to be readily cleaved upon treatment with bis(cyclooctadiene)nickel(0) to give the aryl(arenethiolato)-nickel(II) complex 6 by oxidative addition as shown in eq. 17.[27] This discovery is extremely important in understanding the carbon-sulfur bond reduction promoted by organonickel reagent. The metal-alkyl bond thus formed would probably undergo inter- or intramolecular reductive elimination with metal-hydride to give the corresponding reduced product.

$$Ni(COD)_2 + ArSAr + 2PEt_3 \longrightarrow ArNi(SAr)(PEt_3)_2 + 2COD \quad (17)$$

6

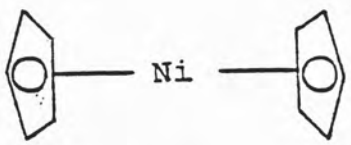
Metal hydride can also be formed by the reduction of a metal halide with lithium aluminum hydride.[28] Mukaiyama and his coworkers reported that, upon treatment with lithium aluminum hydride, both cupric chloride (eq. 18)[29] and titanium(IV) chloride (eq. 19)[30] are effective desulfurization agents. Presumably, both reactions may involve metal hydride as intermediate.

$$Ph_2CHSPH \xrightarrow[THF,\text{reflux } 3 \text{ h}]{2(CuCl_2 + 2LiAlH_4)} Ph_2CH_2 \quad (18)$$

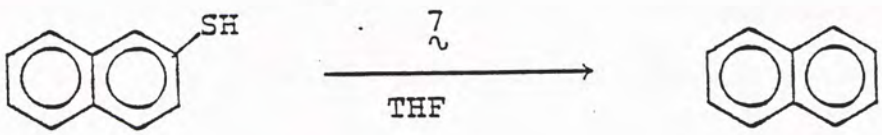


(19)

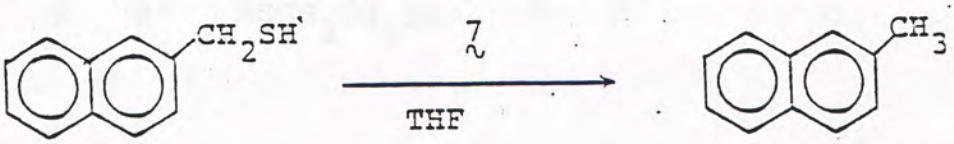
Recently, an effective desulfurization reagent 7 prepared from nickelocene (8) and lithium aluminum hydride was uncovered in this laboratory. In a preliminary study,[31] it was shown that aryl or benzylic mercaptans and thioethers were readily reduced (eqs. 20 and 21). The reaction behavior seems to be quite similar to that of Raney nickel.[8] In this thesis, a detail investigation of this newly developed reagent 7 is presented. The stability of various functional groups under the reaction conditions has been studied. Preliminary mechanistic study on this intriguing reaction has been carried out.*



8



9 10 (20)



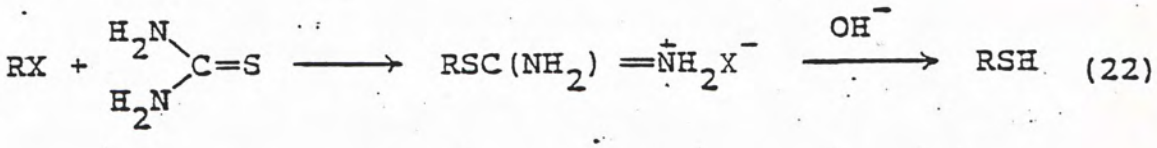
11 12 (21)

* Part of this work has been published in a preliminary communication (cf Ref 32).

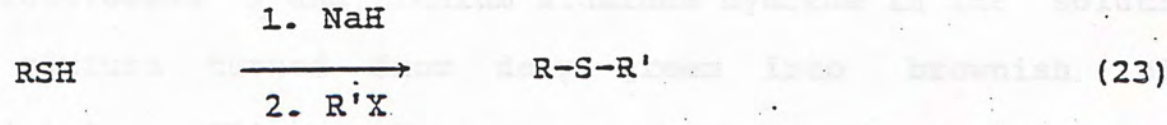
RESULTS AND DISCUSSION

Synthesis

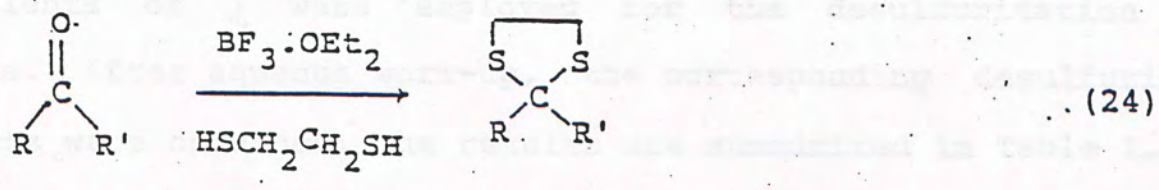
The mercaptans 16-21, thioether 13 as well as thioketals 3,22,23 used in this study were prepared according to eqs. 22-24, respectively.[33,34] The details are described in the EXPERIMENTAL SECTION.



(22)



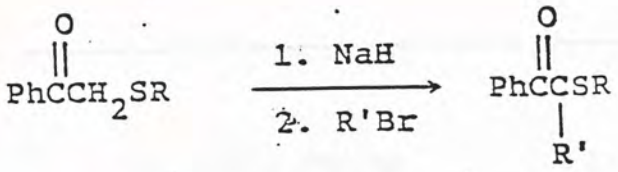
(23)



(24)

Compound 14 was prepared from the allylation of 13a. The

alkyne derivative 15 was similarly synthesized from 13b (eq. 25).



(25)

13a R= CH_3 14 R= CH_3 R'= $H_2C{=}CHCH_2$

b R= Ph 15 R= Ph R'= $HC{\equiv}CCH_2$

Desulfurization study

The reagent 7 was prepared by mixing an equal molar amount of nickelocene 8 and Lithium aluminum hydride in THF solution. The mixture turned from deep green into brownish black immediately. This solution was then treated with various organosulfur compounds at ambient temperature unless otherwise specified. In general, one equivalent of the nickel reagent 7 is required for each carbon-sulfur bond reduced. Thus, two equivalents of 7 were employed for the desulfurization of sulfide. After aqueous work-up, the corresponding desulfurized products were obtained. The results are summarized in Table 1.

As shown in Table 1, the yields for these reactions are moderate to good. Various kinds of carbon-sulfur bond can readily be reduced under these conditions.

Table 1. Desulfurization of Organosulfur compounds with 7.

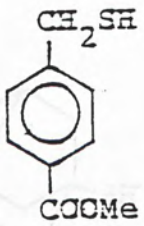
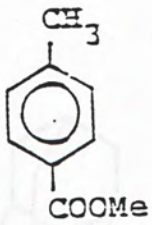
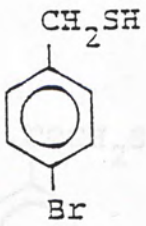
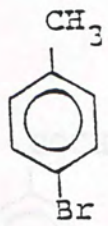
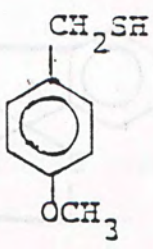
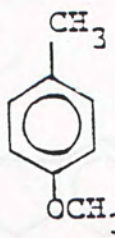
Substrate	Substrate: Cp_2Ni:$LiAlH_4$	Product	%Yield
$CH_3(CH_2)_8CH_2SH$ 16	1:2:2	$CH_3(CH_2)_8CH_3$ 24	41[a]
 17	1:1:1	 25	40
 18	1:1:1	 26	25
 19	1:1.4:1.4	 27	36

Table 1 (cont'd)

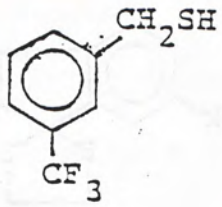
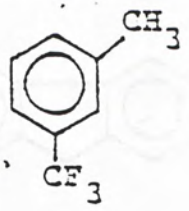
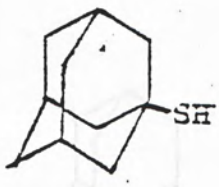
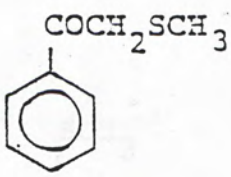
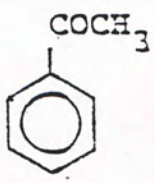
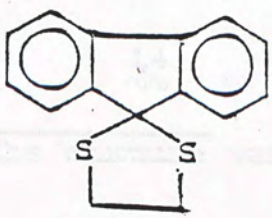
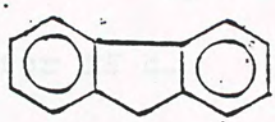
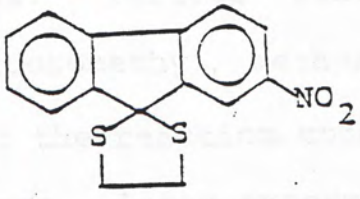
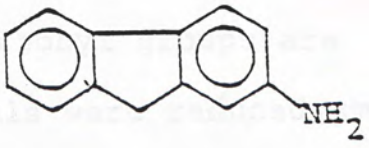
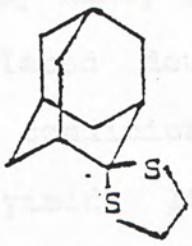
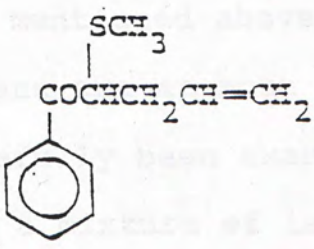
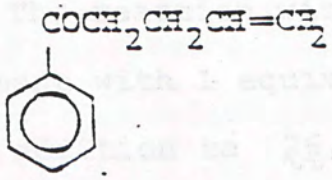
Substrate	Substrate: Cp_2Ni:$LiAlH_4$	Product	%Yield
 20	1:1:1	 28	34
 21	1:2:2	 29	46[a]
 13	1:2:2	 30	74
 3	1:8:8	 31	55

Table I (cont'd)

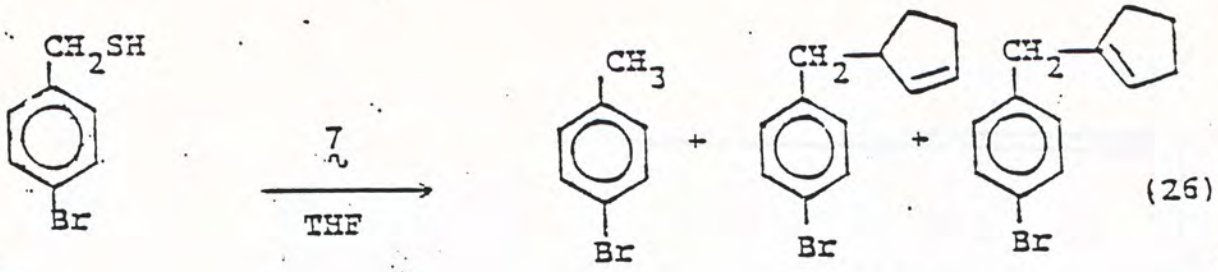
Substrate	Substrate: Cp_2Ni:$LiAlH_4$	Product	%Yield
 22	1:8:8	 32	40
 23	1:4:4	 29	22[a]
 14	1:2.5:2.5	 33	78

a. The mixture was heated under reflux for 16 h.

In general, aliphatic or alicyclic carbon-sulfur bonds are less reactive. Thus, elevated temperature was employed for the reactions with 16, 21 and 23. Substituted benzylic thiols 17-20 afforded the corresponding reduced products 25-28 in moderate yields. Various functional groups such as methoxy, bromo, trifluoromethyl, methoxycarbonyl and carbonyl groups are stable under the reaction conditions. Thioketals were reduced smoothly. However, large excess amount of the reagent 7 was used in order to give satisfactory yield. In the presence of excess 7, nitro group was also reduced to amino group. Hence 32 was obtained in 40% yield from 22. It is noted that nitro group can also be reduced by Raney nickel.[8]

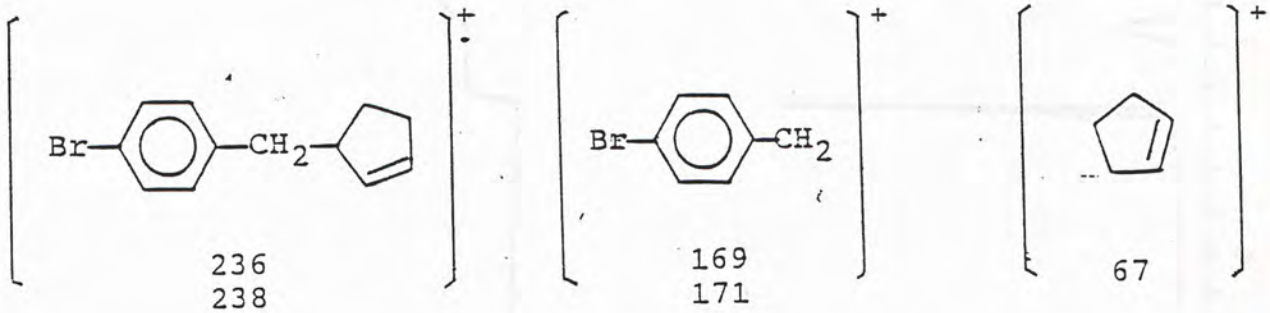
Isolated double bond was found to be stable under the reaction conditions. To illustrate, the reduction of 14 gave 33 in 78% yield. It is worth to mention that double bond in 14 was neither reduced nor rearranged. The high yield of this substrate may be due to the presence of α-acyl group which may stabilize the intermediate. In a similar manner, good yield was obtained from the reduction of 13.

As mentioned above, the yields for the reduction of benzylic mercaptans are at most moderate (Table 1). The reaction with 18 has carefully been examined. Thus, on treatment with 1 equivalent of 7, a mixture of isomers 34 and 35, in addition to 26, was obtained (eq. 26). Attempts to separate 34 and 35 were



18 26 34 35

unsuccessful. The mass spectral fragments for the mixture 34 and 35 are shown below:



It is clear that both 34 and 35 retained the p-bromobenzyl moiety. The nmr spectrum for this mixture is shown in Figure 1. The singlets at δ5.35 and δ3.30 are assigned to the absorptions of the olefinic and benzylic protons in 35, respectively. The absorptions of olefinic protons for 34 appear at δ5.60-5.80 as multiplet. The incorporation of cyclopentene moiety into the products 34 and 35 is intriguing. The possible mechanism for the formation of these products will be discussed later.

Attempts to desulfurize 15 were unsuccessful, and only a mixture of unidentified products was obtained.

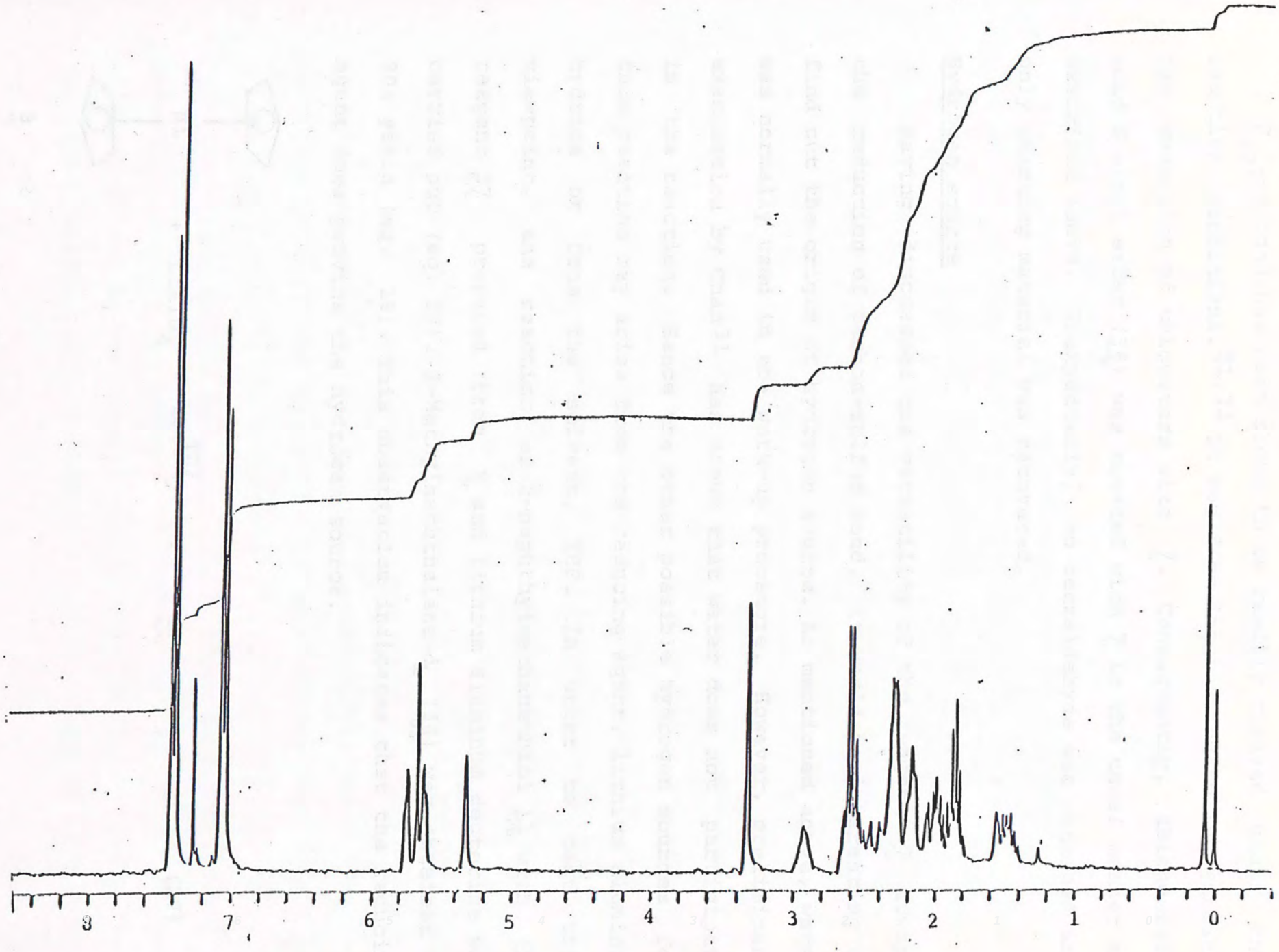


Figure 1. ^{1}H-nmr spectrum for 34 and 35.

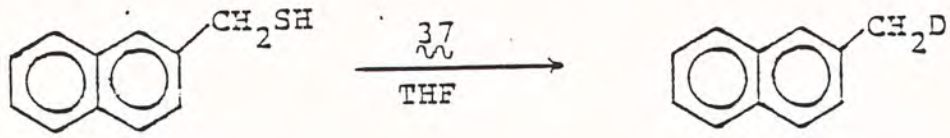
C_{sp^2}-S bond has been shown to be readily cleaved under the reaction conditions.[31,32] It would be interesting to investigate the reduction of thioesters with 7. Consequently, thiobenzoic acid S-ethyl ester (36) was treated with 7 in the usual manner as described above. Unexpectedly, no benzaldehyde was obtained and only starting material was recovered.

Hydrogen source

Having discusssed the versatility of the reagent 7 toward the reduction of carbon-sulfur bond, it would be interesting to find out the origin of hydrogen source. As mentioned above, water was normally used in the work-up procedure. However, preliminary examination by Chan[31] has shown that water does not participate in the reaction. Hence the other possible hydrogen sources for this reaction may arise from the reducing agent, lithium aluminum hydride or from the solvent, THF. In order to test this viewpoint, the reaction of 2-naphthylmethanethiol 11 with the reagent 37 prepared from 8 and lithium aluminum deuteride was carried out (eq. 27). 2-Methylnaphthalene-d_1 (38) was obtained in 80% yield (eq. 28). This observation indicates that the reducing agent does provide the hydrogen source.

Ni + $LiAlD_4$ $\xrightarrow{THF}$ 37 (27)

8



(28)

11 38

The Nature of the Reagent

As described in the previous paragraph the hydridic species may play an important role in the reduction of carbon-sulfur bond under these conditions. Earlier study by Chan[31] suggested that lithium aluminum hydride has been consumed because the reagent 7 exhibited no absorption between 1600-2200 cm^{-1} in the infrared region. This finding is further confirmed by the study of ^{1}H-nmr spectrum of 7 (see below).

The ^{13}C-nmr spectrum of 7 in THF-d_8 has been measured (Figure 2). Interestingly, only one peak at 104.4 ppm over the range from -100 to 240 ppm appears in this spectrum. This signal is assigned to the absorption of symmetrically coordinated η^5-cyclopentadienyl carbons.[35] It is noted that nickelocene 8 is paramagnetic[36] and does not exhibit absorption in the region mentioned above. Since there is only one peak in the ^{13}C-nmr spectrum, it is clear that the cyclopentadienyl moiety remains attached to some kind of metallic species during the course of the preparation of the reagent 7. In other words, no liberation of the organic ligand was observed.

The ^{1}H-nmr spectra for 7 and 37 are shown in Figures 3 and 4 respectively. It is noteworthy that, in addition to the absorption due to cyclopentadienyl protons at δ5.80, there are two broad singlets at δ1.90 and δ2.40 which disappear in the ^{1}H-

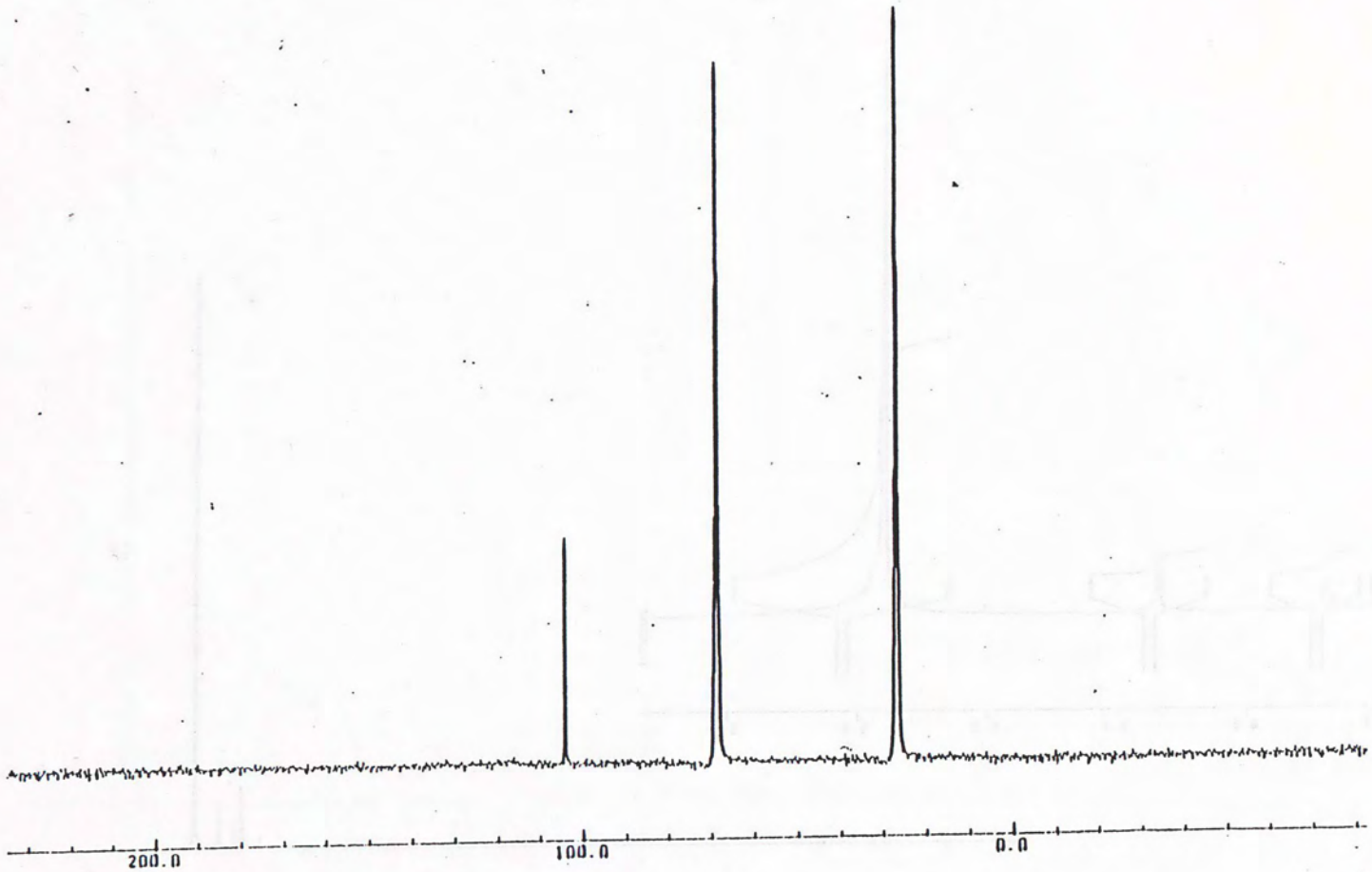


Figure 2. ^{13}C-nmr spectrum for 7 in THF-d_8.

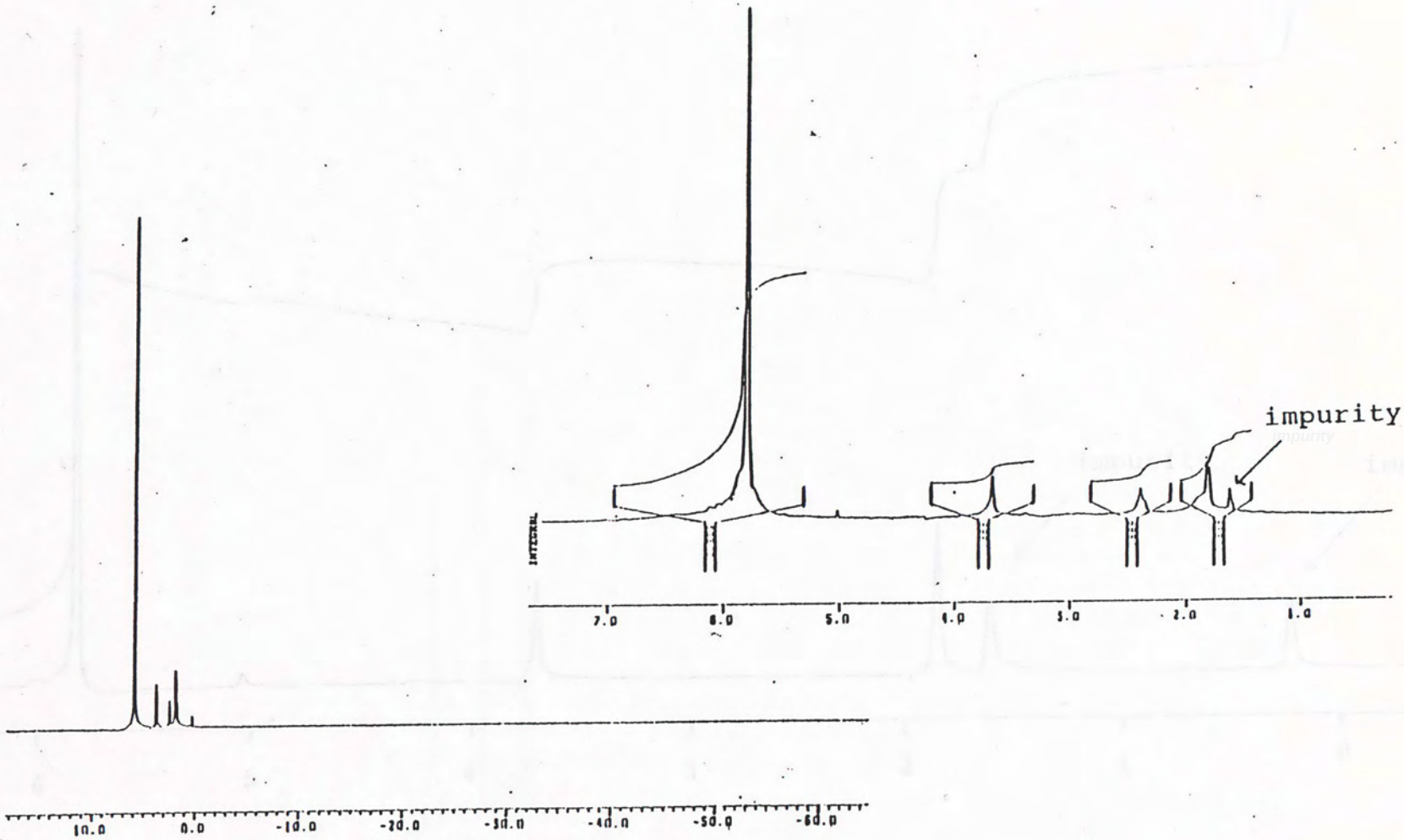


Figure 3. ^{1}H-nmr spectrum for 7 in THF-d_8.

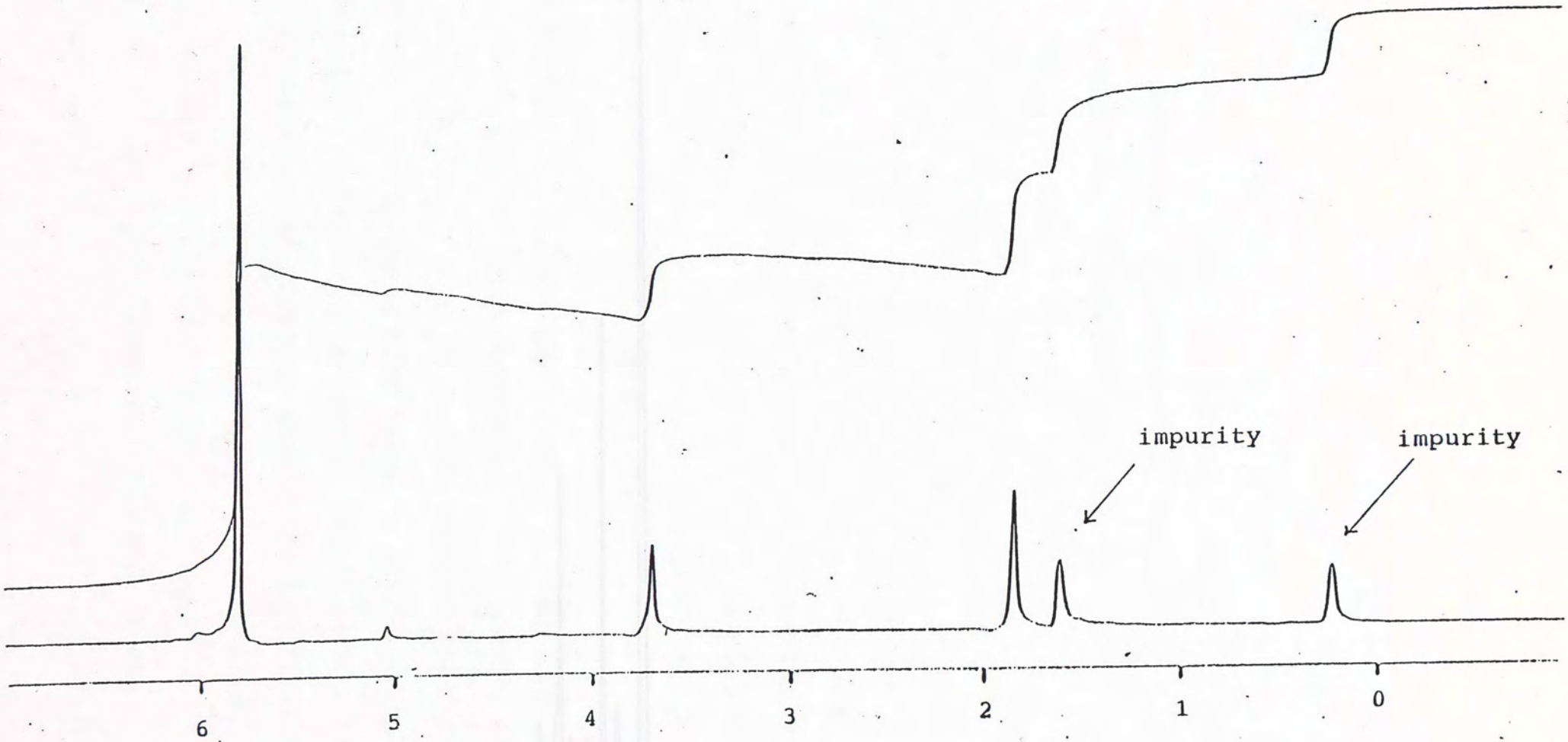


Figure 4. ^{1}H-nmr spectrum for 37 in THF-d_8.

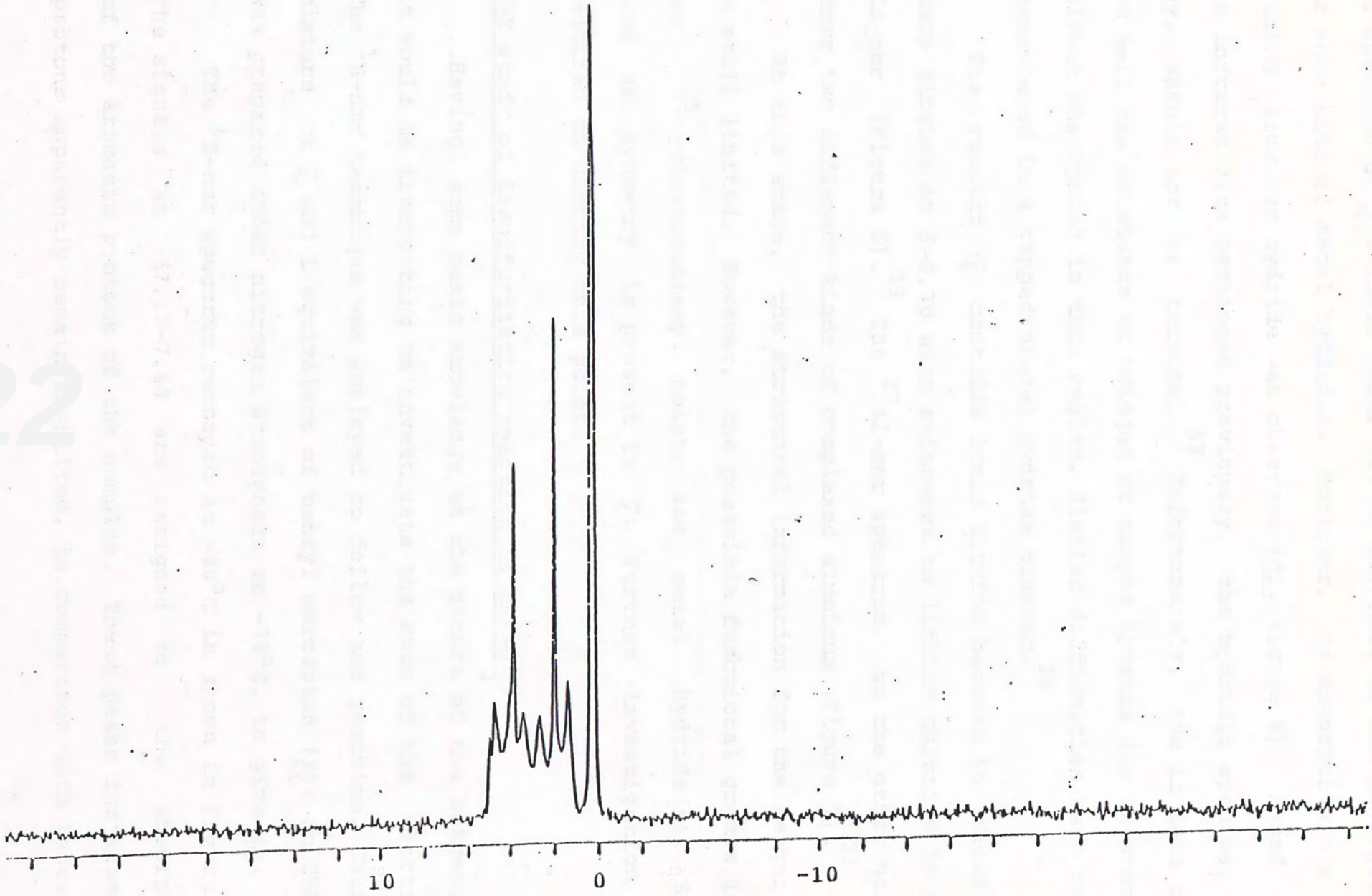


Figure 5. ^{1}H-nmr spectrum for lithium aluminum hydride in THF-d_8.

nmr spectrum of 37. These peaks may be ascribed as the absorption for some kind of metal hydrides. Moreover, no absorption due to Lithium aluminum hydride was observed (cf. Figure 5). Based on the infrared data mentioned previously, the hydridic species, if any, should not be terminal.[37] Unfortunately, the ir data can not tell the existence of bridged or capped hydride due to strong solvent absorption in this region. Similar difficulties have been encountered in a capped nickel hydride cluster.[38]

The reagent 7 contains ionic lithium because it shows a sharp singlet at δ-6.70 with reference to lithium chloride in the ^{7}Li-nmr (Figure 6).[39] The ^{27}Al-nmr spectrum, on the other hand, shows two different kinds of complexed aluminum (Figure 7).[39]

At this stage, the structural information for the reagent 7 is still limited. However, the posssible functional groups in 7 are η^5-cyclopentadienyl moiety and metal hydride(s). Some kind of symmetry is present in 7. Further investigation is required to clarify this point.

NMR study of desulfurization reaction in THF-d_8

Having some basic knowledge on the nature of the reagent 7, it would be interesting to investigate the mode of the reaction. The ^{1}H-nmr technique was employed to follow the reaction. Thus, a mixture of 7 and 1 equivalent of benzyl mercaptan (39) in THF-d_8 was prepared under nitrogen atmosphere at -78°C. to give 40.

The ^{1}H-nmr spectrum recorded at -80°C is shown in Figure 8. The signals at δ7.10-7.60 are assigned to the absorption of the aromatic protons of the complex. These peaks for aromatic protons apparently remain unshifted, in comparison with those for

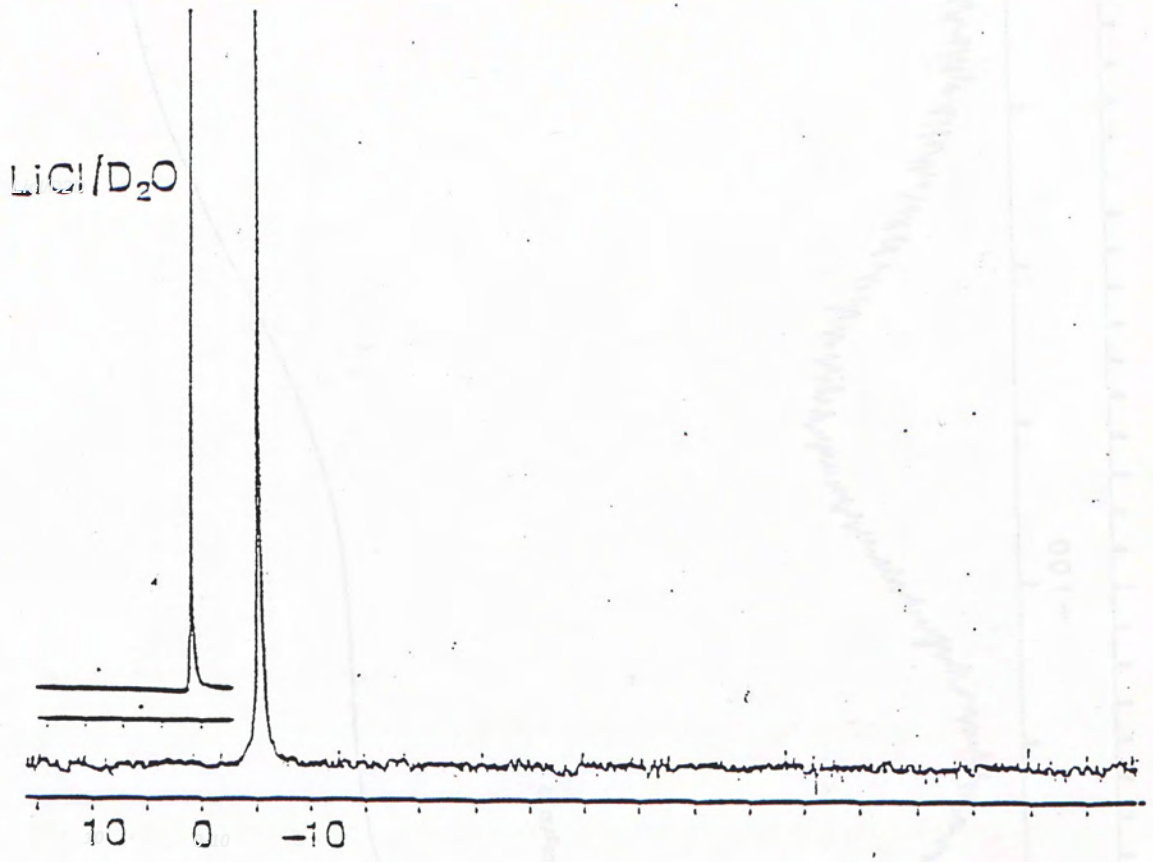


Figure 6. ^{7}Li-nmr spectrum for 7 in THF-d_3.

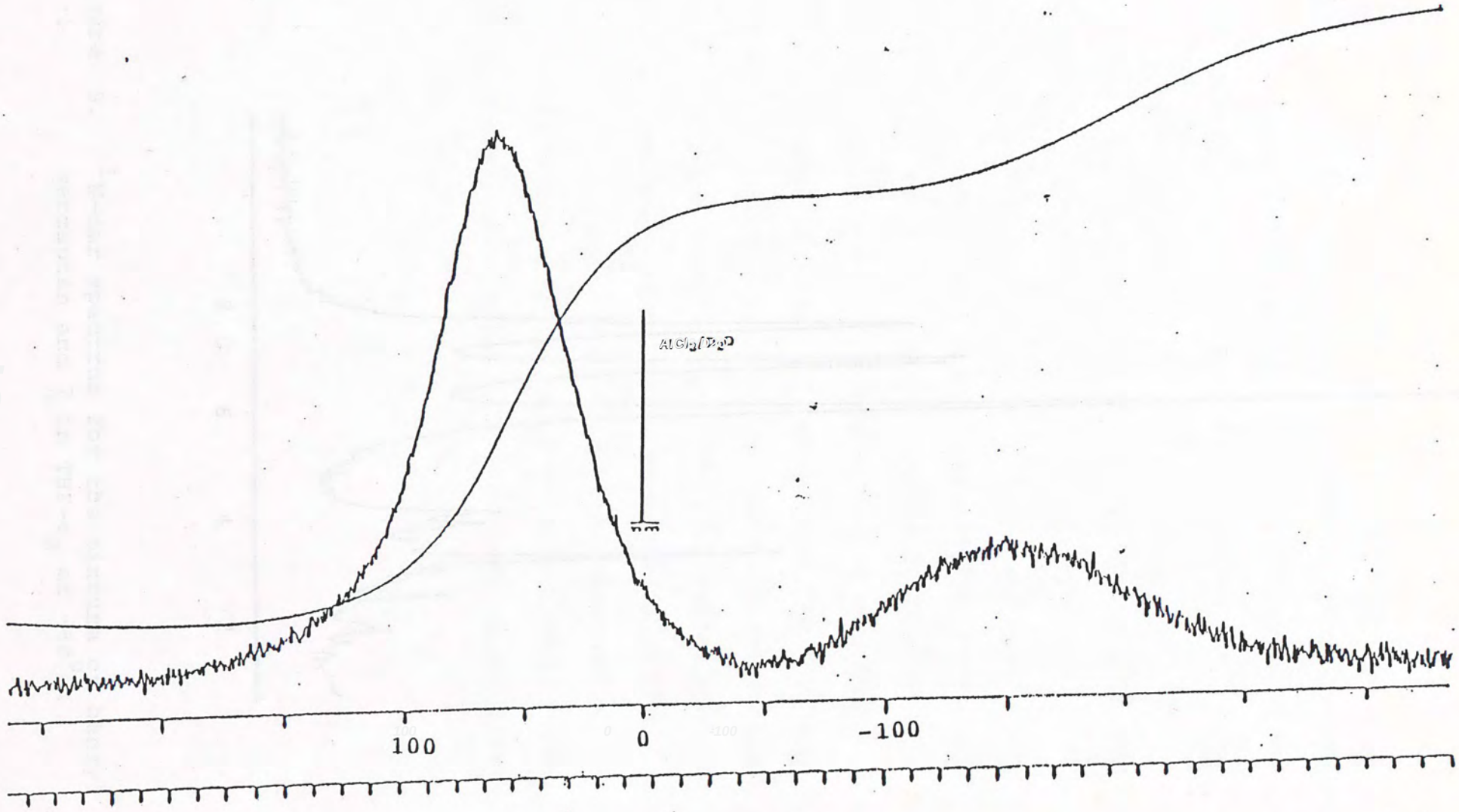


Figure 7. ^{27}Al-nmr spectrum for 7 in THF-d_8.

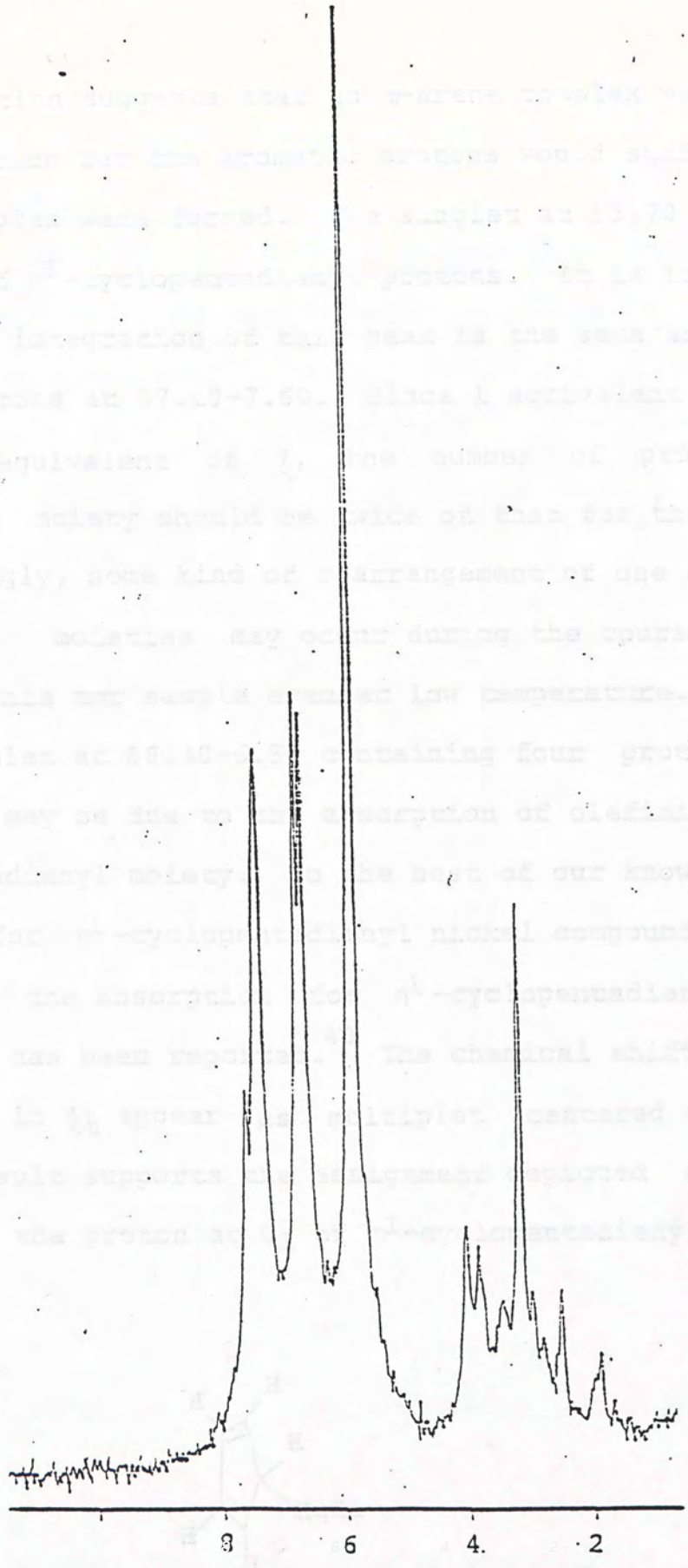
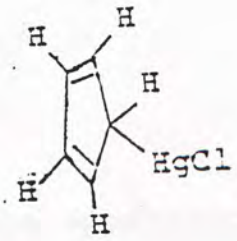


Figure 8. ^{1}H-nmr spectrum for the mixture of benzyl mercaptan and $\underset{\sim}{7}$ in THF-d_8 at -80°C.

39. This observation suggests that no π-arene complex was formed, since the absorption for the aromatic protons would shift upfield if such π-complex were formed. The singlet at δ5.70 is due to the absorption of η^5-cyclopentadienyl protons. It is interesting to note that the integration of this peak is the same as that for the aromatic protons at δ7.10-7.60. Since 1 equivalent of 39 was mixed with 1 equivalent of 7, the number of protons for cyclopentadienyl moiety should be twice of that for the aromatic moiety. Accordingly, some kind of rearrangement of one of the η^5-cyclopentadienyl moieties may occur during the course of the preparation of this nmr sample even at low temperature. There is a complex multiplet at δ6.40-6.50 containing four protons. This set of signals may be due to the absorption of olefinic protons in η^1-cyclopentadienyl moiety. To the best of our knowledge, the nmr spectrum for η^1-cyclopentadienyl nickel compounds is not known. However the absorption for η^1-cyclopentadienylmercuric chloride (41) has been reported.[40] The chemical shifts for the olefinic proton in 41 appear as multiplet centered at δ6.61 at -96°C. This result supports the assignment depicted above. The absorption for the proton at C_1 of η^1-cyclopentadienyl moiety in

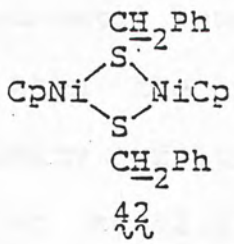
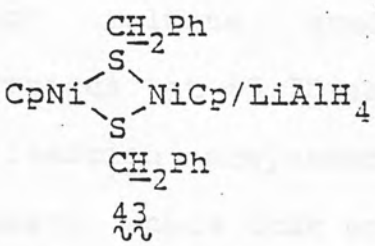


41

40 should appear at higher field and may be embodied in the residual solvent peaks.

The singlet appearing at δ3.00 is interesting. This peak may arise from the absorption of the benzylic methylene protons. The chemical shift for these methylene protons is compared with those of related compounds as outlined in Table 2.

Table 2. Chemical shifts of methylene protons of derivatives of benzyl mercaptan.

Substrate	δ
$PhC\underline{H}_2SH$ (39)	3.70
 (42)	3.30
 (43)	3.05
$PhC\underline{H}_2SH/Cp_2Ni/LiAlH_4$ (40)	3.00

It is noted that the appearance of the methylene protons in the reaction mixture exhibited at much higher field in comparison with that of benzyl mercaptan and with that of complexed benzyl thiolato compound 42.[41] Furthermore, the chemical shift for the

methylene protons of 43 prepared from 42 and lithium aluminum hydride shifted upfield to δ3.05. Presumably some kinds of hydridic species which may be formed in the latter reaction may cause the upfield shift for methylene protons in 42.[41] Since the organosulfur moiety is ligated to nickel in 42 and in 43, it is reasonable to suggest that the benzyl mercaptan may also form complex with 7. As a result, the chemical shift for such methylene protons exhibited at higher field as shown in Table 2. It is believed that such complex formation would be important for the cleavage of carbon-sulfur bond. It is noteworthy that the carbon-sulfur bond has recently been found to be weakened in certain thiolato complexes.[42] Furthermore, the carbon-sulfur bond has been found undergoing oxidative addition with a nickel(0) complex (eq. 17).[27] However, the formation of the corresponding carbon-metal bond was not detected in this study.

When the mixture was warmed up to room temperature, the intensity of the signal at δ3.00 gradually decreased and a new singlet at δ2.31 due to the absorption of methyl protons of the product, toluene, gradually appeared (Figure 9). Meanwhile, the absorptions at δ5.70 and at δ6.40-6.50 gradually diminished. As the reaction prolonged, the concentration of the complex decreased while that of toluene increased (Figure 9). Based on the results so far obtained, a possible mechanism for the desulfurization reaction with the reagent 7 is proposed and outlined in Scheme 4.

As mentioned above, the reagent 7 may contain bridged or capped hydride(s) and one kind of η^5-cyclopentadienyl moiety. The

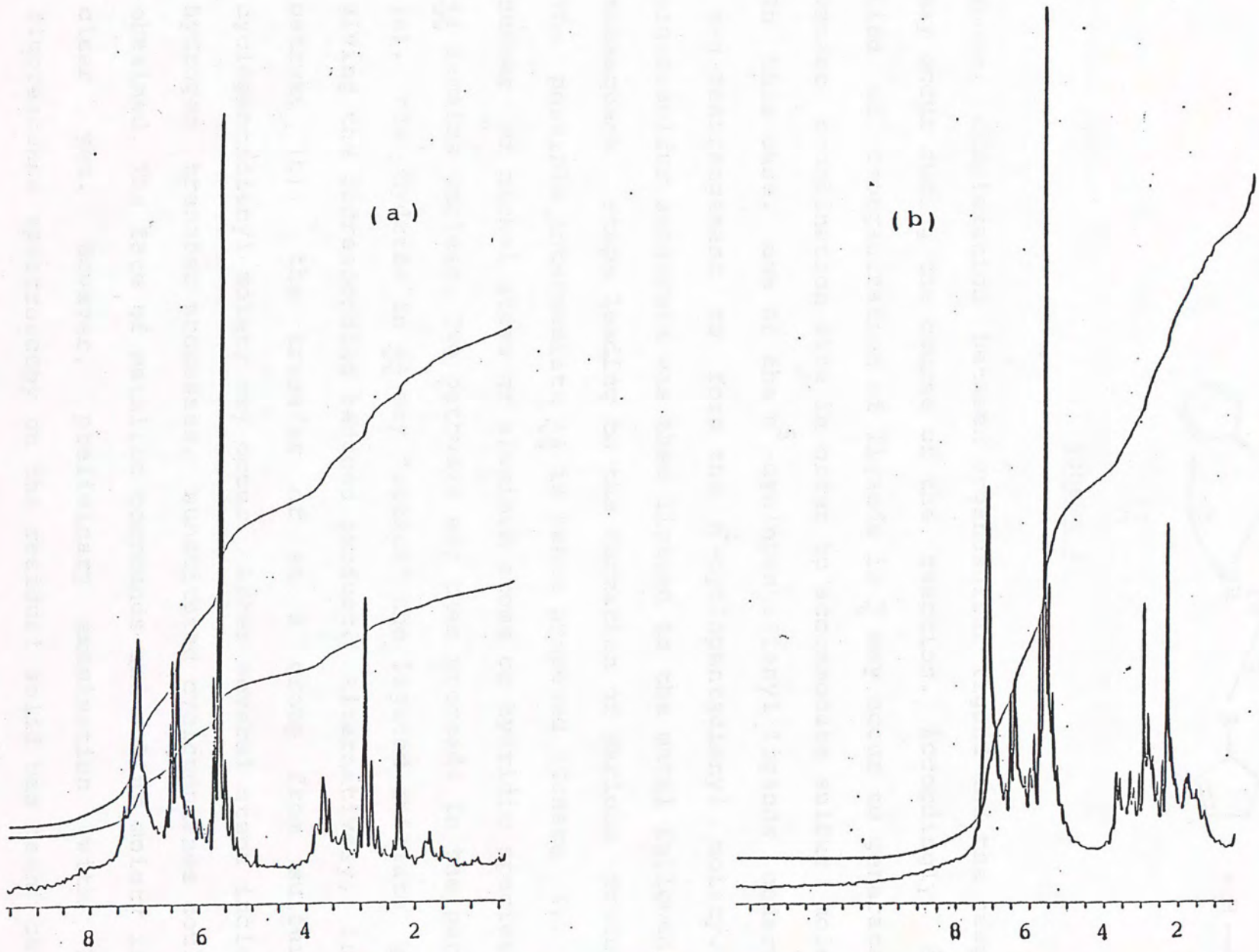
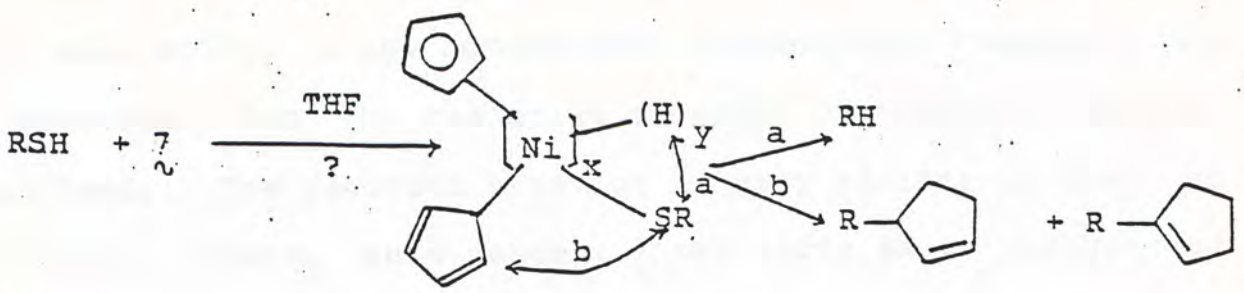


Figure 9. ^{1}H-nmr spectra for the reaction of benzyl mercaptan and 7 in THF-d at ambient temperature after 12h (a) and 24h (b).

metal center in 7 may be coordinatively saturated. As discussed



44

Scheme 4

above, complexation between organosulfur ligand and the reagent may occur during the course of the reaction. Accordingly, some kind of reorganization of ligands in 7 may occur to generate a vacant coordination site in order to accommodate sulfur moiety. In this case, one of the η^5-cyclopentadienyl ligands underwent π-σ rearrangement to form the η^1-cyclopentadienyl moiety. The organosulfur substrate was then ligated to the metal followed by subsequent steps leading to the formation of various products. The possible intermediate 44 is hence proposed (Scheme 4). The number of nickel atoms or aluminum atoms or hydridic species in 44 remains unclear. Two pathways may then proceed. In the pathway (a), the hydride in 44 may "attack" the ligated thiolato group giving the corresponding reduced product. Alternatively, in the pathway (b), the transfer of an R group from sulfur to cyclopentadienyl moiety may occur. After several steps including hydrogen transfer processes, substituted cyclopentenes could be obtained. The fate of metallic compounds and sulfur moiety is not clear yet. However, preliminary examination with X-ray fluorescence spectroscopy on the residual solid has been carried out. Sulfur, nickel and aluminum have been detected.

CONCLUSION

In this study, a new homogeneous organonickel reagent 7 has been developed for the reductive cleavage of various carbon-sulfur bonds. The reaction behavior is very similar to that of Raney nickel. Hence, this reagent 7 may serve as a homogeneous model for the study of the mechanism of reaction promoted by Raney nickel. Preliminary mechanistic study of the reaction with 7 suggests that metal hydride(s) may play a significant role in the reduction of carbon-sulfur bonds. This observation supports the earlier studies[9,10] that interstitial hydrogen(s) may provide the hydrogen source for the reduction of carbon-sulfur bonds. More detailed mechanistic studies would be required to explore the actual mode of these important reactions.

EXPERIMENTAL

Melting points (mp) and boiling points (bp) are uncorrected. Nuclear magnetic resonance (nmr) spectra were recorded on JEOL 60-HL (60 MHz) and Bruker WM250 nmr (250 MHz) spectrometers. Mass spectra (ms) were determined on a VG-7070F mass spectrometer. Infrared spectra were measured on a Perkin-Elmer 283 infrared spectrophotometer. Gas chromatography was operated on a Hewlett-Packard 700 vapor fractometer.

All reactions were performed under nitrogen atmosphere using standard inert gas operation techniques.[43,44] Tetrahydrofuran (THF) was distilled from potassium sodium alloy/benzophenone prior to use.[43-45] Other solvents were distilled before use.[44] Nickelocene,[46] 1-adamantanethiol,[47] 3-trifluorophenylmethanethiol,[48] 2-nitrofluorenone[49] were prepared according to literature procedures.

1-Decanethiol (16).[50] To a 250-mL round bottom flask containing 1-bromodecane (22.1g, 0.1 mol), was added a solution of thiourea (9.9g, 0.13 mol) in aqueous ethanol (70%, 30 mL). The mixture was refluxed for 2 h. After cooling, an aqueous solution of sodium hydroxide (10%) was added and the resulting mixture was refluxed with stirring for a further 2 h and cooled to room temperature. The organic layer was separated and the aqueous layer was acidified and then extracted with ether. The combined organic solution was dried with anhydrous magnesium sulfate, filtered, and the filtrate was evaporated in vacuo to give the residue which was distilled to afford 1-decanethiol (13.2g, 76%): bp. 66-68°C (1.2 mm; lit.[50] 96-97°C, 5mm) ^{1}H-nmr($CDCl_3$): δ 0.80-

1.70(20H,m), 2.50 (2H,q,J=7.5Hz).

2-Bromomethylnaphthalene (45). A mixture of 12 (50g, 0.35 mole), azobisisobutyronitrile (AIBN) (ca. 0.1g) and N-bromosuccinimide (63g, 0.37 mol) in carbon tetrachloride (500 mL) was refluxed for 3 h and then cooled to room temperature. After filtration, the filtrate was evaporated in vacuo to give the residue which was distilled to give 45 (70g, 90%): bp. 110-112° (0.05 mm); mp. 50-51°C, (lit.[51] mp. 54°C).

2-Naphthylmethanethiol (11). In a similar manner described for the preparation of 16, 45 (20g, 0.09 mol) and thiourea (8.4g, 0.11 mol) were transformed into 11 (9g, 57%): mp. 47-48°C. (lit.[52] mp. 47.2-47.7°C).

4-Methoxycarbonyl-α-bromotoluene (46). By employing the similar method for the preparation of 45, 25 (50g, 0.33 mol), AIBN (ca. 0.1g) and N-bromosuccinimide (65g, 0.37 mol) were transformed into 46, as colorless needles (49g, 65%): mp. 48-50°C (petroleum ether, lit.[53] mp. 54-55°C); ^{1}H-nmr($CDCl_3$): δ3.85(3H,s), 4.40(2H,s), 7.25-8.05(4H,m).

4-Mercaptomethylbenzoic acid (47). In a similar manner as described for the preparation of 16, 46 (26.5g, 0.12 mol) and thiourea (9.2g, 0.12 mol) were converted to 47 (5g, 25%): mp. 175-178°C (EtOH; lit.[54] mp. 179-180°C); ^{1}H-nmr($CDCl_3$): δ2.90(1H,t,J=7.5Hz), 3.85(2H,d,J=7.5Hz), 7.45-8.15(4H,m).

4-Methoxycarbonylphenylmethanethiol (17). Compound 48 (5g, 0.03 mol) was dissolved in methanol (100 mL), to which concentrated

sulfuric acid (1 mL) was added. The mixture was refluxed overnight, cooled to room temperature, poured into ice water and then extracted with ether. The organic solution was washed with water, dried with anhydrous magnesium sulfate and filtered. The filtrate was evaporated in vacuo and the residue was distilled to give 17 (2g, 37%): bp. 78-80°C (0.65 mm); ^{1}H-nmr($CDCl_3$): δ1.80(1H,t,J=7.5Hz), 3.70(2H,d,J=7.5Hz), 3.85(3H,s), 7.15-8.05(4H,m); ms: m/e 182.0393 (calcd for $C_9H_{10}O_2S$: 182.0401).

4-methoxy-α-bromotoluene (48). In a similar manner as described for the preparation of 45, a mixture 27 (30g, 0.25 mol), AIBN (ca 0.1g) and N-bromosuccinimide (43.7g, 0.25 mol) was converted to 48 (45.5g, 92%): bp. 80-84°C (1 mm; lit.[55] 105-10°C, 8mm).

4-Methoxyphenylmethanethiol (19). In a similar procedure as described for the preparation of 16, 48 (21g, 0.1 mol) and thiourea (7.6g, 0.1 mol) were transformed into 19 (6g, 38%): bp. 60-62°C (0.1 mm), (lit.[56] 89-94°C, 2.5 mm); ^{1}H-nmr($CDCl_3$): δ1.70(1H,t,J=7.5Hz), 3.55(2H,d,J=6Hz), 3.65(3H,s), 6.97(4H,m).

α,4-dibromotoluene (49). In a similar manner as described for the preparation of 44, 26 (60g, 0.35 mol), AIBN (ca 0.1g) and N-bromosuccinimide (65g, 0.38 mol) were converted to 49 (47g, 54%); mp. 58-60°C (lit.[57] mp. 60-62°C).

4-Bromophenylmethanethiol (18). In a similar manner as described for the preparation of 16, 49 (20g, 0.08 mol) and thiourea (6.2g, 0.08 mol) were transformed into 18 (6g, 37%): mp. 26-28°C (lit.[58] mp. 25-27°C); ^{1}H-nmr($CDCl_3$): δ1.70 (1H,t, J=7.5 Hz), 3.57(2H,d, J=7.5Hz), 7.00-7.50(4H,m).

2,2-Ethylenedithioadamantane (23). A mixture of adamantanone (6g, 0.04 mol), 1,2-ethanedithiol (10 mL, 0.12 mol) and boron trifluoride etherate (10 mL, 0.08 mol) in hot acetic acid (150 mL) was heated under reflux for 2 h. The mixture was cooled and let stand for crystallization. After filtration, the solid was recrystallized from chloroform-acetone affording 23 as colorless leaflets (4.2g, 46%): mp. 56-57°C (lit.[59] 55-56°C); ^{1}H-nmr($CDCl_3$): δ1.50-2.30 (14H,m), 3.20 (4H,s).

9,9-Ethylenedithiofluorene (3). In a similar manner as described for the preparation of 23, fluorenone (9g, 0.05 mol), 1,2-ethanedithiol (15 mL, 0.18 mol) and boron trifluoride etherate (15 mL, 0.12 mol) were converted to 16 as colorless rods (9g, 70%): mp. 126-127°C ($CHCl_3$-MeOH; lit.[60] mp. 125°C); ^{1}H-nmr($CDCl_3$): δ3.75(4H,s), 7.15-7.85(8H,m).

9,9-Ethylenedithio-2-nitrofluorene (22). In a similar way as described for the preparation of 23, a mixture of 2-nitrofluorenone (2g, 9 mmol), 1,2-ethanedithiol (5 mL, 0.06 mol) and boron trifluoride etherate (2 mL, 0.016 mol) was transformed into 22 (1.9g, 70%): mp. 231-234°C; ^{1}H-nmr($CDCl_3$): δ3.82(4H,s), 7.28-7.50(2H,m,$H_{7,8}$), 7.65-7.78(3H,m,H_{4-6}), 8.23(1H,d,J=10Hz,H-3), 8.52 (1H,d,J=3.8Hz,H_1); ms: m/e 301.0229 (calcd for $C_{15}H_{11}NO_2$: 301.0231).

α-Methylthioacetophenone (13). Sodium hydride (3g, 80% dispersed in oil, 0.1 mol) in a three-necked round bottom flask, fitted

with a cold finger and a dry-ice cooled addition funnel, was washed with petroleum ether three times under nitrogen atmosphere. THF (150 mL) was then introduced and the mixture was cooled to ca. -78°C. Methylmercaptan (condensed at -78°C, ca. 15 mL) was then added dropwisely and the mixture was gradually warmed to room temperature. A solution of α-bromoacetophenone (20g, 0.1 mol) in THF (30 mL) was added and the reaction mixture was stirred overnight under nitrogen and then poured into water (100 mL), and extracted with ether (4 X 20 mL). The ethereal solution was dried, filtered and the filtrate was evaporated in vacuo to give the residue which was distilled to afford 13 (12.5g, 75%): bp. 82-86°C (0.1 mm; lit.[61] bp. 100-105°C, 0.4 mm); nmr($CDCl_3$): δ2.10(3H,s), 3.75(2H,s), 7.40-8.10(5H,m).

α-Methylthio-α-allylacetophenone (14). Sodium hydride (80%, 0.8g, 0.027 mol) in a three-necked round bottom flask was first washed with petroleum ether three times under nitrogen atmosphere. THF (150 mL) was introduced and the mixture was cooled to ca. -78°C. Compound 13 (4.2g, 0.025 mol) was then added dropwisely and the mixture was gradually warmed to room temperature. A solution of allyl bromide (4.5g, 0.037 mol) in THF (30 mL) was then added and the reaction mixture was stirred overnight under nitrogen, poured into water (100 mL), extracted with ether (4 X 20 mL). The ethereal solution was dried, filtered and the filtrate was evaporated in vacuo to give the residue which was distilled to afford 14 (4.45g, 86%); bp. 78-82°C (0.08 mm); ^{1}H-nmr($CDCl_3$): δ1.90(3H,s), 2.30-2.90(2H,m), 4.22(1H,t,J=7.5Hz), 4.90-5.35(2H,m), 5.40-6.30(1H,m), 7.10-8.00(5H,m); ms: m/e 206.0743 (calcd for $C_{12}H_{14}OS$: 206.0765).

α-Phenylthio-α-propargylacetophenone (15). In a similar mannar as described for the preparation of 14, a mixture of sodium hydride (80%, 0.5g, 0.017 mol), α-phenylthioacetophenone (3g, 0.013 mol) and propargyl bromide (1.6g, 0.013 mol) was transformed into 15 (2.6g, 74%): mp. 104-106°C; ^{1}H-nmr ($CDCl_3$): δ2.00-2.20(1H,m), 2.70-2.90(2H,m), 4.70(1H,t,J=7.5Hz), 7.4-8.3(9H,m); ms: m/e 266.0743 (calcd for $C_{17}H_{14}OS$: 266.0765).

Thiobenzoic acid S-ethylester (36). A mixture of benzoyl chloride (5g, 0.03 mol), pyridine (5 mL) and ethyl mercaptan (3.72g, 0.06mol) was allowed to react at 0°C for 1 h and then at room temperature overnight. Water was then added and the mixture was extracted with ether. The organic solution was washed with hydrochloric acid (10%) and then with water, dried over anhydrous magnesium sulfate, filtered and the filtrate was evaporated in vacuo to give 36 (2.4g, 46%): bp. 146-148°C (30 mm; lit.[62] bp. 128-130°C, 12mm); ^{1}H-nmr($CDCl_3$): δ1.30 (3H,t,J=6.75Hz), 3.05(2H,q,J=7.5Hz), 7.10-8.10(5H,m).

General procedure for desulfurization reaction. A THF solution (50 mL) of nickelocene (8) (1g, 5.3 mmol) was added to lithium aluminum hydride (0.2g, 5.3 mmol) in THF (20 mL) and the mixture was stirred for 15 min to give a brownish black mixture 7. A THF solution (30 mL) of equimolar of sulfur-containing substrate (5.3 mmol) was then added dropwisely to the above mixture. After stirring under nitrogen at room temperature for 12-24 h, the reaction was quenched with water (20 mL), filtered and the filtrate was extracted with ether (4 X 40 mL). The organic solution was dried over anhydrous magnesium sulfate, filtered,

and the filtrate was evaporated in vacuo to give the residue which was chromatographed on silica gel.

Desulfurization of 4-methoxycarbonylphenylmethanethiol (17). According to the general procedure, a mixture of 8 (0.52g, 2.8 mmol), lithium aluminum hydride (0.11g, 2.9 mmol), and 17 (0.45g, 2.5 mmol) was reduced to 25 (0.14g, 40%) which showed identical spectroscopic properties with those of the authentic sample.

Desulfurization of 4-methoxyphenylmethanethiol (19). By using the general procedure, a mixture of 8 (0.98g, 5.2 mmol) and lithium aluminum hydride (0.19g, 5.2 mmol) in THF (50 mL) and 19 (0.57g, 3.7 mmol) was converted to 27 (0.16g, 36%) which was characterized by comparing its spectroscopic properties with those of the authentic sample.

Desulfurization of 4-bromophenylmethanethiol (18). A mixture of 8 (0.53g, 2.8 mmol), lithium aluminum hydride (0.11g, 2.9 mmol) in THF (50 mL), and 18 (0.57g, 2.8 mmol) was allowed to react in the usual manner as described above. After work-up, the residue was subject to GC analysis. Two peaks were observed on the chromatography. Preparative GC was employed using OV1 column at 110°C to separate these two components. The first fraction was identified as 4-bromotoluene 26 (0.12g, 25%) which showed same physical properties with those of the authentic sample. The second fraction (0.26g, 39%) contained two compounds 34 and 35 based on ^{1}H-nmr (Figure 1) and ms data: ^{1}H-nmr ($CDCl_3$) for 35 δ1.4-2.8(6H,m), 3.30(2H,s), 5.35(1H,m); ^{1}H-nmr ($CDCl_3$) for 34

δ1.4-2.8(6H,m), 2.8-3.0(1H,d), 5.6-5.8(2H,m), 7.0-7.5(4H,m). m/e 236, 238; 169, 171. Attempts to seperate 34 and 35 by chromatographic methods were unsuccessful.

Desulfurization of α-methylthioacetophenone (13). According to the general procedure, a mixture of 8 (2.29g, 12 mmol), lithium aluminum hydride (0.46g, 12 mmol) in THF (50 mL), and 13 (0.84g, 5.1 mmol) was transformed into 30 (0.45g, 74%) which was characterized by comparing its spectroscopic properties with those of the authentic sample.

Desulfurization of α-methylthio-α-allylacetophenone (14). By using the general procedure, a mixture of 8 (0.98g, 5.2 mmol), lithium aluminum hydride (0.2g, 5.3 mmol), and 14 (0.4g, 2 mmol) was transformed into 33 (0.25g, 78%); ^{1}H-nmr($CDCl_3$): δ 2.2-2.70(2H,m), 2.70-3.20(2H,m), 4.75-5.35(2H,m), 5.40-6.30(1H,m), 7.10-8.00(5H,m); ms: m/e 160.

Desulfurization of 9,9-ethylenedithiofluorene (3). By the use of the general procedure, a mixture of 8 (3.0g, 16 mmol), lithium aluminum hydride (0.61g, 16 mmol) and 3 (0.51g, 2mmol) in THF (50 mL) was transformed into 31 (0.18g, 55%): mp. 112-115 °C ; (lit.[63] 115-116 °C).

Desulfurization of 9,9-ethylenedithio-2-nitrofluorene (22). According to the general procedure, 22 (0.25g, 0.82 mmol) was reduced to 32 (0.06g, 40%): mp.125-128 °C; (lit[64] 129 °C).

Desulfurization of thiobenzoic acid S-ethylester (36). Following the general procedure, 36 (0.86g, 5.2 mmol) was treated with 7.

After normal work-up, only starting material was recovered (0.82g, 95%).

Desulfurization of 3-trifluoromethylphenylmethanethiol (20). According to the general procedure, 20 (0.76g, 4 mmol) was transformed to 28 (0.22g, 35%) which exhibited same physical properties with those of the authentic sample.

Desulfurization of 1-decanethiol (16). A mixture of nickelocene 8 (2.27g, 12 mmol) and lithium aluminum hydride (0.54g, 14 mmol) in THF (50 mL) was treated with 16 (1.02g, 6 mmol) in THF (ca. 150 mL) according to the general procedure except that the mixture was refluxed for 16 h to afford 24 (0.172g, 41%) which exhibited identical properties with those of the authentic sample.

Desulfurization of 1-adamantanethiol (21). Following the procedure for the reaction with 16, a mixture of 8 (0.65g, 3.4 mmol), lithium aluminum hydride (0.13g, 3.4 mmol) and 21 (0.26g, 1.5 mmol) in THF (50 mL), was heated under reflux for 16 h followed by normal work-up procedure to give 29 (0.097g, 46%) which showed same physical properties with those of the authentic sample.

Desulfurization of 2,2-Ethylenedithioadamantane (23). Following the procedure for the reaction with 16, a mixture of 8 (0.87g, 4.6 mmol) and lithium aluminum hydride (0.174g, 4.6 mmol) in THF 23 (0.26g, 1.2mmol) in THF (50 mL), was heated under reflux for 16h followed by normal work-up procedure to give 22 (0.034g, 22%).

Desulfurization of 2-naphthylmethanethiol (11) with 37 in THF The reaction was carried out in a manner as discerned in the general procedure except that lithium aluminum deuteride was used instead of lithium aluminum hydride. Thus 11 (0.61g, 3.5 mmol) was transformed to 38 (0.40g, 80%); m/e 143.

NMR study of the reagent 7 in THF-d_8. Under nitrogen atmosphere, a solution (2.0 mL) of 8 (34mg, 0.18 mmol) was added to lithium aluminum hydride (6.8mg, 0.18 mmol) in THF-d_8 (1.0 mL) in an nmr tube. The mixture was shaken for 15 min at room temperature. The nmr tube was then sealed and subject to nmr analysis.

NMR study of the reaction of benzyl mercaptan (39) with 7 in THF-d_8. Under nitrogen atmosphere, a solution (0.5 mL) of 8 (0.079g, 0.4 mmol) was added to lithium aluminum hydride (16mg, 0.4 mmol) in THF-d_8 (0.5 mL) in an nmr tube. The mixture was shaken for 15 min at room temperature. A THF-d_8 solution (0.5 mL) of 41 (52mg, 0.4 mmol) was then added dropwisely to the above mixture under nitrogen at -78°C. The nmr tube was then sealed and subject to nmr analysis.

REFERENCES

1. Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978.

2. Oae, S. "Organic Chemistry of Sulfur"; Plenum: New York, 1977.

3. Trost, B. M.; Melvin, Jr., L. S. "Sulfur Ylides: Emerging Sythetic Intermediates"; Academic Press: New York, 1975.

4. Djerassi, C.; Gorman, M.; Henry, J. A. J. Chem. Soc. 1955, 77, 4647.

5. Luh. T.-Y.; Lei, K.-L. J. Chem. Soc., Chem. Commun. 1981, 214. J. Org. Chem. 1981, 46, 5328;

6. Carruthers, W.; Douglas, A. G. J. Chem. Soc. 1959, 2813.

7. (a) Gassman, P. G.; Gilbert, D. P.; Luh, T.-Y. J. Org. Chem. 1977, 42, 1340.
   (b) Gassman, P. G.; van Bergen, T. J. J. Am. Chem. Soc. 1974, 96, 5508.

8. (a) Pettit, G. R.; van Tamelen, E. E. Org. React. 1962, 12, 356.
   (b) Hauptmann, H.; Walter, W. F. Chem. Rev. 1962, 63, 347.

9. (a) Bonner, W. A. J. Am. Chem. Soc. 1952, 74, 1034.
   (b) Hauptmann, H.; Wladislaw, B. J. Am. Chem. Soc. 1950, 72, 707, 711.

10. Horner, L.; Doms, G. Phosphorus Sulfur 1978, 4, 259.

11. (a) Mitchell, P.C.H. Catalysis 1981, 4, 175.
    (b) Clausen, B. S.; Lengeler, B.; Topsøe, H. Polyhedron 1986, 5, 199 and references therein.
    (c) Eltzner, W.; Breysse, M.; Lacroix, M.; Vrinat, M. Polyhedron 1986, 5, 203 and references therein.

12. Parshall, G. W. "Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes"; Wiley: New York, 1980.

13. Alper, H.; Blais, C. Fuel 1980 59, 670.

14. Brignole, A. B.; Cotton, F. A. Inorg. Synth. 1972, 13, 87.

15. Alper, H.; Blais, C. J. Chem. Soc., Chem. Comm. 1980, 169.

16. Luh, T.-Y.; Wong, C. S. J. Org. Chem. 1985, 50, 5413.

17. Wong, C. S.; Leung, W. S.; Yeung, L. L.; Luh, T.-Y. J. Organomet. Chem. 1986, 307, C49.

18. Alper, H.; Paik, H. N. J. Org. Chem. 1977, 42, 3522.

19. Alper, H.; Shim, S. C.; Antebi, S. Tetrahedron Lett. 1985, 26, 1935.

20. (a) Shim, S. C.; Antebi, S.; Alper, H. J. Org. Chem. 1985, 50, 147.
(b) Antebi, S.; Alper, H. Organometallics 1986, 5, 596.

21. Alper, H. J. Org. Chem. 1975, 40, 2694.

22. Alper, H.; Sibtain, F.; Heveling, J. Tetrahedron Lett. 1983, 24, 5329.

23. (a) Eisch, J. J.; Hellenbeck, L. E.; Han, K. I. J. Org. Chem. 1983, 48, 2963.
(b) Eisch, J. J.; Im, K. R. J. Organomet. Chem. 1977, 139, C51.

24. (a) Okamura, H.; Takei, H. Tetrahedron Lett. 1979, 20, 3425.
(b) Wenkert, E.; Ferreira, T. W.; Michelotti, E. L. J. Chem. Soc., Chem. Commun. 1979, 637.
(c) Takei, H.; Sugimura, H.; Miura, M.; Okamura, H. Chem. Lett. 1980, 1209.

25. Wenkert, E.; Ferreira, T. W. J. Chem. Soc., Chem. Commun. 1982, 840.

26. Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, 1980.

27. Osakada, K.; Maeda, M.; Nakamura, Y.; Yamamoto, T.; Yamamoto, A. J. Chem. Soc., Chem. Commun. 1986, 442.

28. (a) Kaesz, H. D.; Saillant, R. B. Chem. Rev., 1972, 72, 231.
(b) Geoffrey, G. L.; Lehman, J. R. Adv. Inorg. Chem. Radio Chem. 1977, 29, 189.

29. Mukaiyama, T.; Narasaka, K.; Maekawa, K.; Furusato, M. Bull. Chem. Soc., Japan 1971, 48, 2285.

30. Mukaiyama, T.; Hayashi, M.; Narasaka, K. Chem. Lett. 1973, 291.

31. Chan, M.-C.; B. Sc. Thesis, The Chinese University of Hong Kong, 1985.

32. Chan, M.-C.; Cheng, K.-M.; Li, M. K.; Luh, T.-Y. J. Chem. Soc., Chem. Commun. 1985, 1610.

33. Vogel, A. I. "A Textbook of Practical Organic Chemistry", 4th Ed.; Longman, 1978, p. 582.

34. Fieser, L. F. J. Am. Chem. Soc. 1954, 76, 1945.

35. Mann, B. E.; Taylor, B. F. "^{13}C NMR Data for Organometallic Compounds" Academic Press: New York, 1981.

36. Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1974, Vol. I, p. 421.

37. Jesson, J. P. In "Transition Metal Hydrides"; Muetterties, E. L. Ed.; Marcel Dekker: New York, 1971.

38. (a) Huttner, G.; Lorenz, H. Chem. Ber. 1974, 107, 996.
(b) Koetzle, T. F.; Muller, J.; Tipton, D. L.; Hart, D. W.; Bau, R. J. Am. Chem. Soc. 1979, 101, 5631.
(c) Koetzle, T. F.; McMullan, R. K.; Bau, R.; Hart, D. W.; Teller, R. G.; Tipton, D. L.; Wilson, R. D. Adv. Chem. Ser. 1978, 67, 61.

39. Harris, R. E.; Mann, B. E. "NMR and the Periodic Table"; Academic Press: London, 1978.

40. West, P.; Woodville, M. C. J. Am. Chem. Soc. 1969, 91, 5649.

41. Ho, N.-F; Mak, T. C. W.; Luh, T.-Y., submitted for publication.

42. (a) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A. J. Am. Chem. Soc. 1986, 108, 1358.
(b) Adams, R. D.; Horvath, I. T.; Mathur, P.; Segmuller, B. E. Organometallics 1983, 2, 996.
(c) Adams, R. D.; Horvath, I. T.; Kim, H.-S. Organometallics 1984, 3, 548.

43. Shriver, D. F. "The Manipulation of Air-sensitive Compounds"; McGraw-Hill: New York, 1969.

44. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Oxford, 1980.

45. Eisch, J. J. "Organometallic Synthesis"; Academic Press: New York, 1981; Vol. II, p. 24.

46. King, R. B. "Organometallic Synthesis"; Academic Press: New York, 1965; Vol. I, p. 72.

47. Geigy, J. R. Belgium Patent, 1963, 629,371. Chem. Abstr. 1964, 60, 9284.

48. Paquette, L. A.; Wittenbrook, L. S.; Schreiber, K. J. Org. Chem. 1968, 33, 1080.

49. Kuhn, W.E. Org. Syn. 1943, Coll. 2, 447.

50. Urquhart, G. G.; Gates, Jr., J. W.; Connor. R. Org. Syn. 1955, Coll. 3, 363.

51. Chapman, N. B.; Williams, J. F. A. J. Chem. Soc. 1952, 5044.

52. Weinstein, H.; Pierson, R. M. J. Org. Chem. 1958, 23, 554.

53. Codington, J. F.; Erich, M. J. Org. Chem. 1952, 17, 1035.

54. Brown, T. M.; Carruthers, W.; Pellatt, M. G. J. Chem. Soc., Perkin Trans. 1 1982, 2, 483.

55. Huyser, E. S. J. Am. Chem. Soc. 1960. 82, 391.

56. Lewis, T. R.; Archer, S. J. Am. Chem. Soc. 1951, 73, 2109.

57. Goerner, G. L.; Nametz, R. J. Am. Chem. Soc. 1951, 73, 2940.

58. Pan, H.-L.; Fletcher, T. L. Chem. Ind. 1968, 17, 546

59. Wilson, S. R; Georgiadis, G. M.; Khatri, H. N.; Bartmess, J. E. J. Am. Chem. Soc. 1980, 102, 3577.

60. Reid, E. E.; Jelinek, A. J. Org. Chem. 1950, 15, 448.

61. Griesbaum, K.; Oswald, A. A.; Hudson, B. E. J. Am. Chem. Soc. 1963, 85, 1969.

62. Cadogan, J. I. G.;Moulden, H. N. J. Chem. Soc. 1961, 5524.

63. Orchin, M. J. Am. Chem. Soc. 1945, 67, 499.

64. Bennett, C. W.; Noyes, W. A. J. Am. Chem. Soc. 1930, 52, 3438.